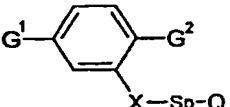




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : C07C 69/92, C09K 19/20, 19/34, 19/38	A1	(11) International Publication Number: WO 00/48985 (43) International Publication Date: 24 August 2000 (24.08.00)
(21) International Application Number: PCT/IB00/00098 (22) International Filing Date: 1 February 2000 (01.02.00) (30) Priority Data: 9903670.9 17 February 1999 (17.02.99) GB (71) Applicant (for all designated States except US): ROLIC AG [CH/CH]; Innere Güterstrasse 2, CH-6301 Zug (CH). (72) Inventors; and (75) Inventors/Applicants (for US only): BUCHECKER, Richard [CH/CH]; 12A Felsenstrasse, CH-8008 Zurich (CH). LUKAC, Teodor [CH/CH]; Oberwilerstrasse 66, CH-4054 Basel (CH). BENECKE, Carsten [DE/DE]; Vierthauen 9, D-79576 Weil Am Rhein (DE). (74) Agent: ENGLAND, Christopher, David; BTG International Limited, 10 Fleet Place, Limeburner Lane, London EC4M 7SB (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: LIQUID CRYSTAL COMPOUNDS <div style="text-align: center;">  <p>(I)</p> </div> (57) Abstract <p>A compound of formula (I), wherein G¹ and G² independently represent a polymerisable mesogenic residue X represents a group selected from the group consisting -CH₂-, -O-, -CO-, -COO-, -OOC-, -CONR'-, -OCOO- and -OCONR'; Sp represents a group of the formula -(CH₂)_p- in which p is an integer of 1 to 18 and in which one or two non adjacent -CH₂- groups are optionally replaced by -CH=CH-; or in which one or two -CH₂- groups may be replaced by one or two groups selected from the group consisting -CH₂-, -O-, -CO-, -COO-, -OOC-, -CONR'-, -OCOO- and -OCONR'- with the proviso that firstly the spacer group does not contain two adjacent heteroatoms and secondly when X is -CH₂-, p can also have a value of 0; Q represents a polar group selected from -CN, -COR, -COOR, -OCOR, -CONR'R, -NR'COR, -OCOOR, -OCONR'R, -NR'COOR, F, Cl, -CF₃, -OCF₃ or -OR or a cyclic group which is unsubstituted or optionally substituted by a group selected from a lower alkyl, lower alkenyl, lower alkoxy, lower alkenyloxy, halogen, -CN, -COR'', -COOR'', -OCOR'', -CONR'R'', -NR'COR'', -OCOOR'', -OCONR'R'', -NR'COOR'', -CF₃, and -OCF₃; where R represents hydrogen, a lower alkyl, a lower alkenyl or a cyclic group as defined above; and R' is hydrogen, a lower alkyl or a lower alkenyl group; R'' represents a lower alkyl or a lower alkenyl group and liquid crystal mixtures containing the compounds.</p>		

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Liquid Crystal Compounds

The present invention relates to laterally substituted curable Liquid Crystals (LCPs) having mesogenic properties or properties which cause these LCPs to be compatible with a mesogenic molecular architecture. In particular the present invention
5 relates to laterally substituted curable Liquid Crystals (LCPs) having a low melting point and good alignment properties and the use of such LCPs in the preparation of substantially uniform or patterned films in which the orientation of the LCP molecules in the plane and relative to the plane of the substrate can be controlled.

Films prepared from curable Liquid Crystals (LCP films) are well known to a
10 skilled person and are used in the preparation of optical and electro-optical devices. These films are generally manufactured by using coating techniques such as spin coating. This involves casting an organic solution of a cross-linkable LCP or LCP mixture onto a substrate provided with an orientation layer. The organic solvent is subsequently removed to give a well orientated, solvent free mesogenic LCP layer. This
15 mesogenic LCP layer may be cross-linked to give a LCP film. The thickness of the LCP film depends upon the viscosity and therefore the concentration of the organic solution of the polymerisable LCP mixture used in the coating process. The uniformity of the film formed depends upon the ability of the LCPs to form homogeneous layers free of tilt domains as well as the stability of the LCP mixture during the coating and cross-
20 linking processes. By the term "tilt domains" it should be understood to mean regions within the LCP film in which the long axis of the LCP molecules form tilt angles with the substrate plane which are of the same size, but have opposite directions.

A problem with known LCPs, especially those having high clearing and melting points, is that they are not able to form mixtures that remain stable during both the
25 coating and cross-linking processes. These prior art LCP mixtures tend to be characterised by a poor solubility in organic solvents; a tendency for the components of the mixture to separate from one another; and a tendency to crystallise. Although attempts have been made to solve these problems by, for example, preparing LCPs with lower melting points, the ability of these prior art LCPs to align with the tilt direction
30 imposed on the film tends to be poor. Such poorly aligned films tend to be characterised by a low contrast ratio.

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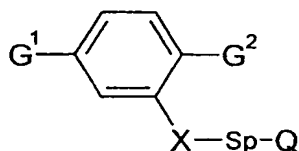
A further problem associated with existing LCP materials is the formation of tilt domains and disclinations during the preparation of LCP films. By the term disclination it should be understood to mean borderlines of neighbouring tilt domains where LCP molecules of opposite tilt angles are adjacent. These tilt domains and disclinations result in both a disturbance in the uniform appearance of the film and an inhomogeneous optical performance.

The aforementioned problems are of particular relevance if photooriented and photopatterned orientation layers are used for the orientation of LCPs. This so called linear photopolymerisation (LPP) technology (*Nature*, 381, p. 212 (1996) allows the production of not only uniform but also structured (photopatterned) orientation layers. If such structured orientation layers are used for the orientation of LCPs, the LCP molecules should adapt the information given by the orientation layer with respect to the direction of alignment and the tilt angle in each single pixel individually.

There is, therefore, a need for a new LCP material that may be used in the preparation of LCP mixtures and layers, which significantly reduces the aforementioned disadvantages and which is especially suitable when applied to LPP orientation layers. The present invention addresses that need.

A first aspect of the invention provides a compound of formula (I)

20



I

wherein

G¹ and G² independently represent a polymerisable mesogenic residue;

25

X represents a group selected from -CH₂-, -O-, -CO-, -COO-, -OOC-, -CONR'-, -OCOO-, -OCONR';

Sp represents a group of the formula -(CH₂)_p- in which p is an integer of 1 to 18 and in which one or two non adjacent -CH₂- groups are optionally replaced by -CH=CH-; or in which one or two -CH₂- groups are

optionally replaced by one or two groups selected from the group consisting -O-, -CO-, -COO-, -OOC-, -CONR'-, -OCOO-, -OCONR'- with the proviso that firstly the spacer group does not contain two adjacent heteroatoms and secondly when X is -CH₂-, p can also have a value of 0;

5

Q represents a polar group selected from -CN, -COR, -COOR, -OCOR, -CONR'R, -NR'COR, -OCOOR, -OCONR'R, -NR'COOR, F, Cl, -CF₃, -OCF₃ or -OR or a cyclic group which is unsubstituted or optionally substituted by a group selected from a lower alkyl, lower alkenyl, lower alkoxy, lower alkenyloxy, halogen, -CN, -COR'', -COOR'', -OCOR'', -CONR'R'', -NR'COR'', -OCOOR'', -OCONR'R'', -NR'COOR'', -CF₃, and -OCF₃;

10

where

15

R represents hydrogen, a lower alkyl, a lower alkenyl or a cyclic group as defined above; and

R' is hydrogen, a lower alkyl or a lower alkenyl group

R'' represents a lower alkyl or a lower alkenyl group.

20

The compounds of the invention have been found to have lower melting points compared to the compounds of the prior art. They have also been found to be more miscible with other components of the liquid crystal mixtures of which they form a part. have a reduced tendency to crystallise from and little effect on the clearing points of such mixtures. In addition they exhibit improved alignment abilities compared to the compounds of the prior art.

25

Laterally substituted mesogenic compounds are known from WO 95/24454, WO 95/24455, US 5,650,534, US 5,593,617, US 5,567,347 and US 5,707,544. However, many of these compounds are not suitable for preparing LCP films and networks that are substantially free of tilt domains. Others exhibit high melting points, higher viscosities (US 5,567,347), lower clearing points (US 5,593,617), poor solubility and/or poor orientation properties. It has been found that by using the compounds of the

30

present invention it is possible to control the orientation or alignment of LCPs or LCP mixtures in the plane of the substrate, to form a tilt angle relative to the plane and to suppress the formation of tilt domains in the mesogenic layers and films formed. The compounds of the invention may therefore be used in the preparation of high contrast
5 optical or electro-optical devices.

The compounds of the invention have also been found to be highly miscible with other LCP compounds over a broad range of concentrations. These compounds and mixtures containing them are extremely soluble in organic solvents. These properties mean that it is possible to prepare coating solutions having a concentration and viscosity
10 that can be controlled over a wide range. Consequently, the thickness of the LCP layers formed using these coating solutions can be readily controlled.

The compounds of the invention are further characterised by relatively low melting points and clearing points that are generally above room temperature. Therefore, during the formation of LCP films or networks using the compounds of the
15 invention or mixtures thereof, spontaneous crystallisation does not tend to occur. This property (otherwise known as supercooling) greatly facilitates the formation of LCP films and networks free of defects. This further means that it is also possible to reduce the number of liquid crystal components used in the manufacture of LCP mixture.

The polymerisable mesogenic residues G^1 and G^2 may be the same or different,
20 but are preferably the same.

The group X is preferably selected from $-CH_2-$, $-O-$, $-COO-$ and $-OOC-$.

The spacer group Sp may be optionally substituted by one or more fluorine atoms. Groups in which there are no substituent groups present are preferred. It is especially preferred that the integer p has a value of from 1 to 11 and that no more than
25 one $-CH_2-$ group is replaced by $-CH=CH-$, $-O-$, $CO-$, $-COO-$, $-OOC-$, $-CONR^1-$, $-OCOO-$, $-OCONR^1$.

The group Q is preferably selected from $-CN$, $-COOR$, $-OCOR$, Cl , $-CF_3$, $-OCF_3$ and $-OR$ in which R is defined as above. The cyclic group may be a saturated or unsaturated, isocyclic or heterocyclic five or six membered cyclic group. The cyclic
30 group may be unsubstituted or may contain one or two substituents independently selected from the group consisting a lower alkyl, lower alkenyl, lower alkoxy, lower

alkenyloxy, halogen, -CN, -COR", -COOR", -OCOR", -CONR'R", -NR'COR", -OCOOR", -OCONR'R", -NR'COOR", -CF₃, -OCF₃ and -OR" in which R' is as defined above and R" represents a lower alkyl or a lower alkenyl group. Preferred halogen substituents for the cyclic group include F and Cl.

5 Preferred five membered cyclic groups included in the group Q are selected from the group consisting of optionally substituted furanyl, tetrahydrofuranyl, dioxolanyl, oxazolyl, 3,4-dihydrooxazolyl and cyclopentyl. Especially preferred five membered cyclic groups include 2-furanyl, 2-tetrahydrofuranyl, 2-dioxolanyl and 3,4-dihydro-2-oxazolyl.

10 Preferred six membered cyclic groups included in the group Q are selected from the group consisting of an optionally substituted phenyl, pyridinyl, pyrimidinyl, cyclohexyl, cyclohexenyl, tetrahydropyranyl, 1,3-dioxanyl. Especially preferred six membered groups include phenyl, cyclohexyl, 1,3-dioxan-2-yl and 2-tetrahydropyranyl.

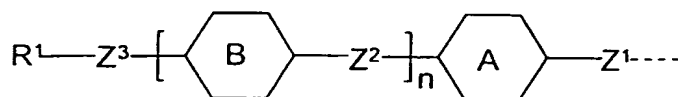
It is preferred that the five or six membered cyclic groups are unsubstituted or
15 contain no more than one substituent group. If a substituent group is present, it is preferably selected from the group consisting of a lower alkyl, lower alkoxy, F, Cl, -CN, -COOR", -OCOR", -OCF₃, OR", in which R" is lower alkyl.

By the term "lower alkyl" it should be understood to include a C₁₋₆ achiral, branched or straight-chained alkyl group. Examples of lower alkyl groups that may be present in
20 the compounds of the invention include methyl, ethyl, propyl, butyl, pentyl hexyl and the like.

By the term "lower alkenyl" it should be understood to include C₃₋₆ achiral, branched or straight-chained alkenyl group in which the double bond is at position 2- or higher. Examples of lower alkenyl groups that may be present in the compounds of the
25 invention include 2-propylene, 3-butylene, 3-isopentylene, 4-pentylene and the like.

By the term "lower alkoxy" it should be understood to include C₁₋₆ achiral, branched or straight-chained alkoxy group. Examples of lower alkoxy groups that may be present in the compounds of the invention include methoxy, ethoxy, propoxy, butoxy, pentoxy, hexoxy and the like.

30 Preferably the polymerisable mesogenic residues G¹ and G² are each independently represented by the group of formula II



II

5 wherein

A and B are independently selected from the group consisting of 1,4-phenylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene and trans-1,3-dioxane-1,4-diyl; optionally substituted with a halogen, -CN, a lower alkyl, lower alkenyl, lower alkoxy or lower alkenyloxy group;

10

n is 1 or 0,

Z^1 and Z^2 are independently selected from the group consisting a single bond, -COO-, -OOC-, -CH₂-CH₂-, -CH₂O-, -OCH₂-, -CH=CH-, -C≡C-,
 15 -(CH₂)₄-, or -(CH₂)₃O-;

Z^3 represents a group of formula -(CH₂)_pX- in which p is an integer having a value of 1 to 18 and X is defined above, and in which one or two non adjacent -CH₂- groups may be optionally replaced by -CH=CH- or in
 20 which one or two -CH₂- groups may be replaced by one or two additional linking groups X with the proviso that firstly the group Z^3 does not contain two adjacent heteroatoms and secondly when X is -CH₂, p can also have a value of 0

25 R^1 represents a polymerisable group selected from the group consisting of CH₂=C(Ph)-, CH₂=CW-COO-, CH₂=CH-COO-Ph-, CH₂=CW-CO-NH-, CH₂=CH-O-, CH₂=CH-OOC-, Ph-CH=CH-, CH₂=CH-Ph-,

$\text{CH}_2=\text{CH}-\text{Ph}-\text{O}-$, $\text{R}^3-\text{Ph}-\text{CH}=\text{CH}-\text{COO}-$, $\text{R}^3-\text{OOC}-\text{CH}=\text{CH}-\text{Ph}-\text{O}-$ and
2-W-epoxyethyl

in which

W represents H, Cl, Ph or a lower alkyl,

5 R^3 represents a lower alkyl with the proviso that when R^3 is attached to a phenylene group (-Ph-) it may also represent hydrogen or a lower alkoxy.

The terms "Ph" and "Ph-" will be understood to indicate a phenyl group, and
10 "-Ph-" any isomer of phenylene, namely 1,2-phenylene, 1,3-phenylene or 1,4-phenylene, except where the context requires otherwise.

The groups A and B may be optionally substituted with a halogen, -CN, a lower alkyl, lower alkenyl, lower alkoxy or lower alkenyloxy group. If a halogen substituent is present this is preferably F or Cl. It is preferred that the groups A and B are selected
15 from optionally substituted 1,4-phenylene and 1,4-cyclohexylene rings. It is especially preferred that the groups A and B are unsubstituted.

By the term "alkenyloxy" it should be understood to include C_{3-6} achiral, branched or straight-chained alkenyloxy group in which the double bond is at position 2- or higher. Examples of lower alkenyloxy groups that may be present in the
20 compounds of the invention include 2-propenyloxy, 3-butenyloxy, 4-pentyloxy, 5-hexenyloxy and the like.

It is preferred that the groups Z^1 and Z^2 are selected from the group consisting a single bond, -COO-, -OOC-, -CH₂-CH₂-, -CH₂O-, -OCH₂-, -CH=CH- and -C≡C-. It is especially preferred that Z^1 and Z^2 represent a single bond, -C≡C-, -COO- or -OOC-.

25 Z^3 may be optionally substituted by one or more halogen atoms, preferably one or more fluorine atoms. It is preferred that p has a value of 1 to 11. It is also preferred that Z^3 contains no substitution. It is further preferred that, for the group Z^3 , X is selected from -CH₂-, -O-, -COO- and -OOC-, especially -CH₂- or -O-.

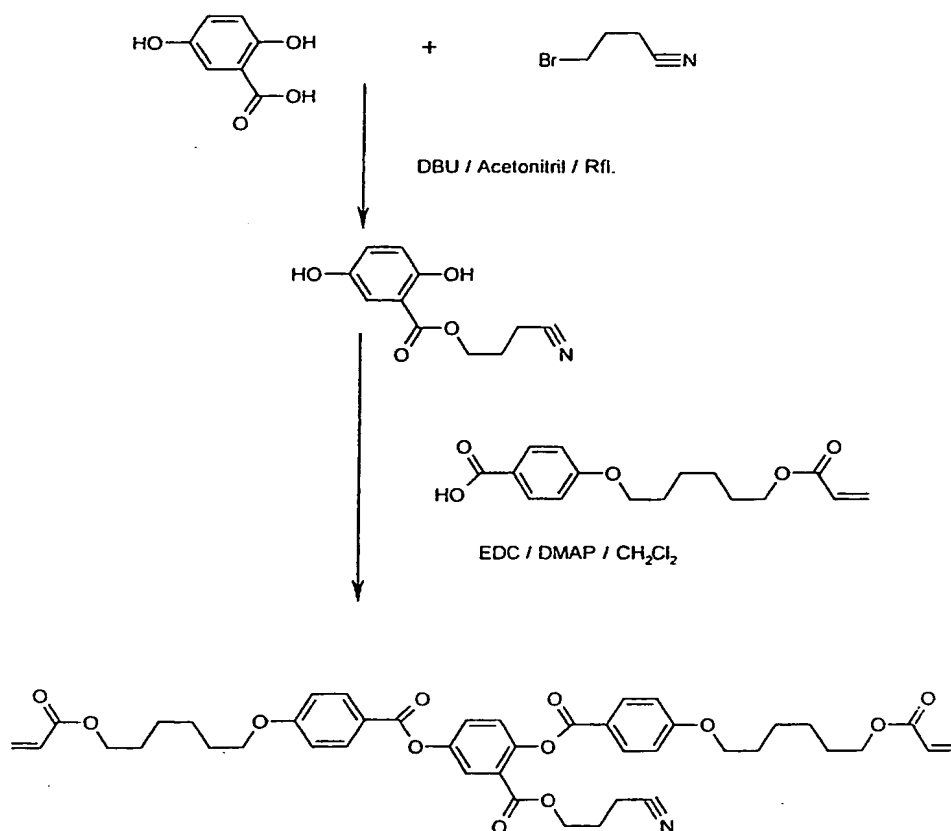
It is preferred that the group R^1 is selected from the group consisting $\text{CH}_2=\text{CW}-$,
30 $\text{CH}_2=\text{CW}-\text{COO}-$ and $\text{CH}_2=\text{CH}-\text{O}-$.

It is preferred that the sum of the two integers n for each of the groups G^1 and G^2 is 0 or 1. It is especially preferred that for both G^1 and G^2 n has a value of 0.

The compounds of the invention may be readily prepared using procedures well known to a skilled person accordance with any one of the procedures set out in Schemes

5 1 to 6 below.

Scheme 1



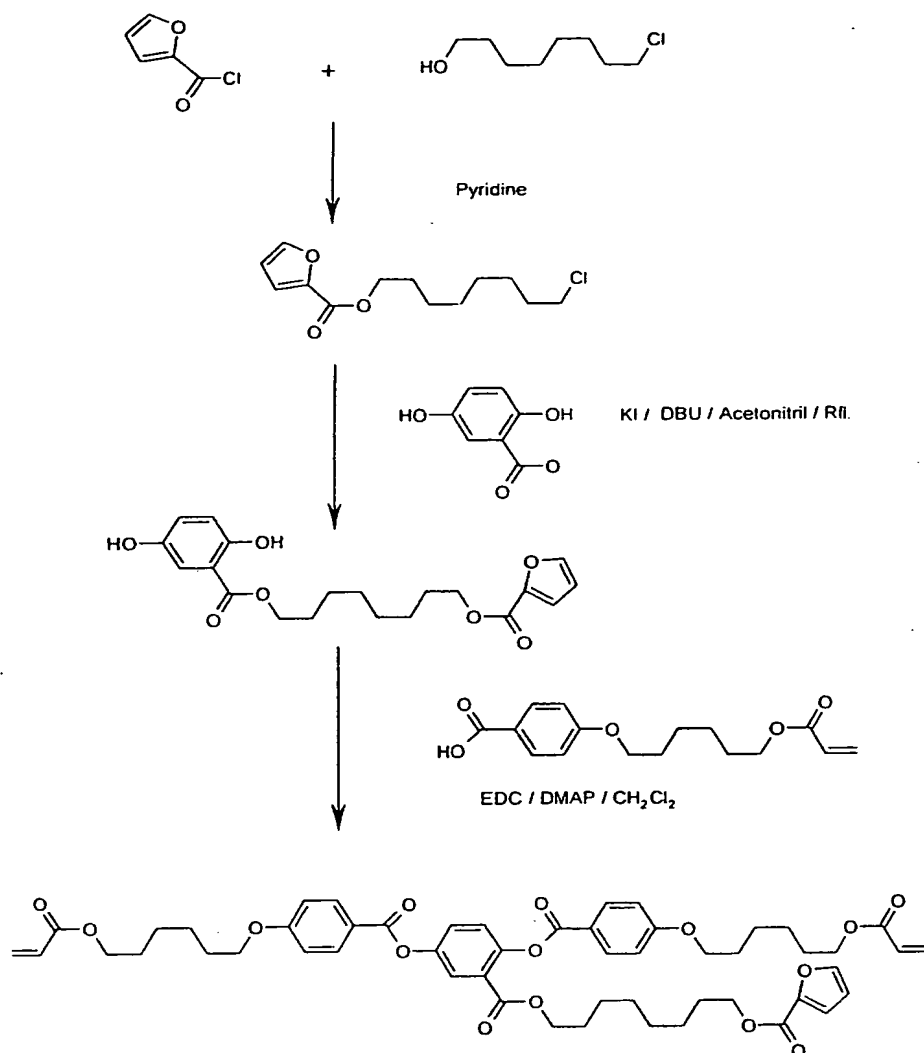
in which :

DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene

10 EDC is N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride

DMAP is 4-dimethylaminopyridine

Scheme 2



in which :

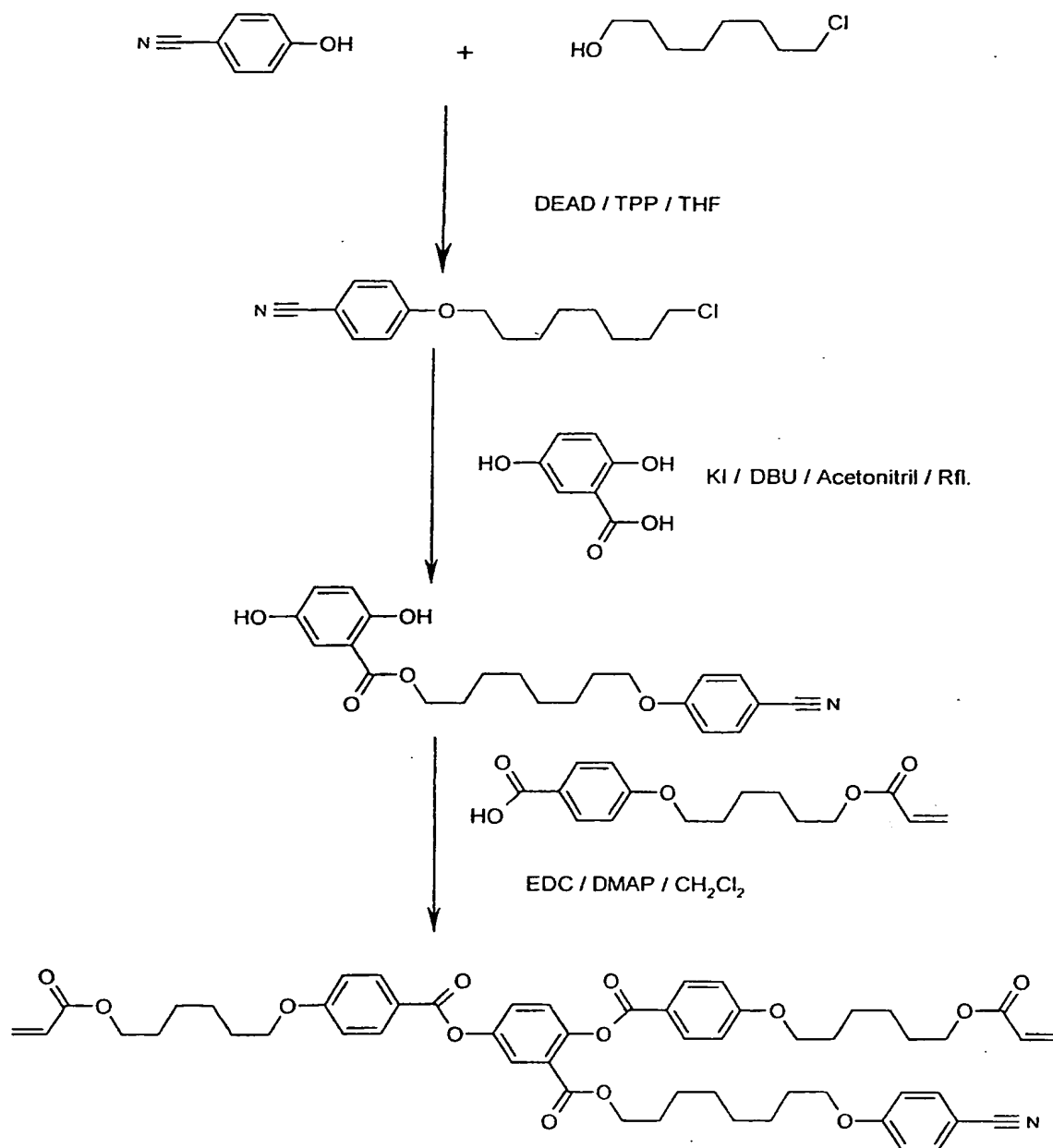
DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene

5 KI is potassium iodide

EDC is N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride

DMAP is 4-dimethylaminopyridine

Scheme 3



in which :

DEAD is diethyl azodicarboxylate

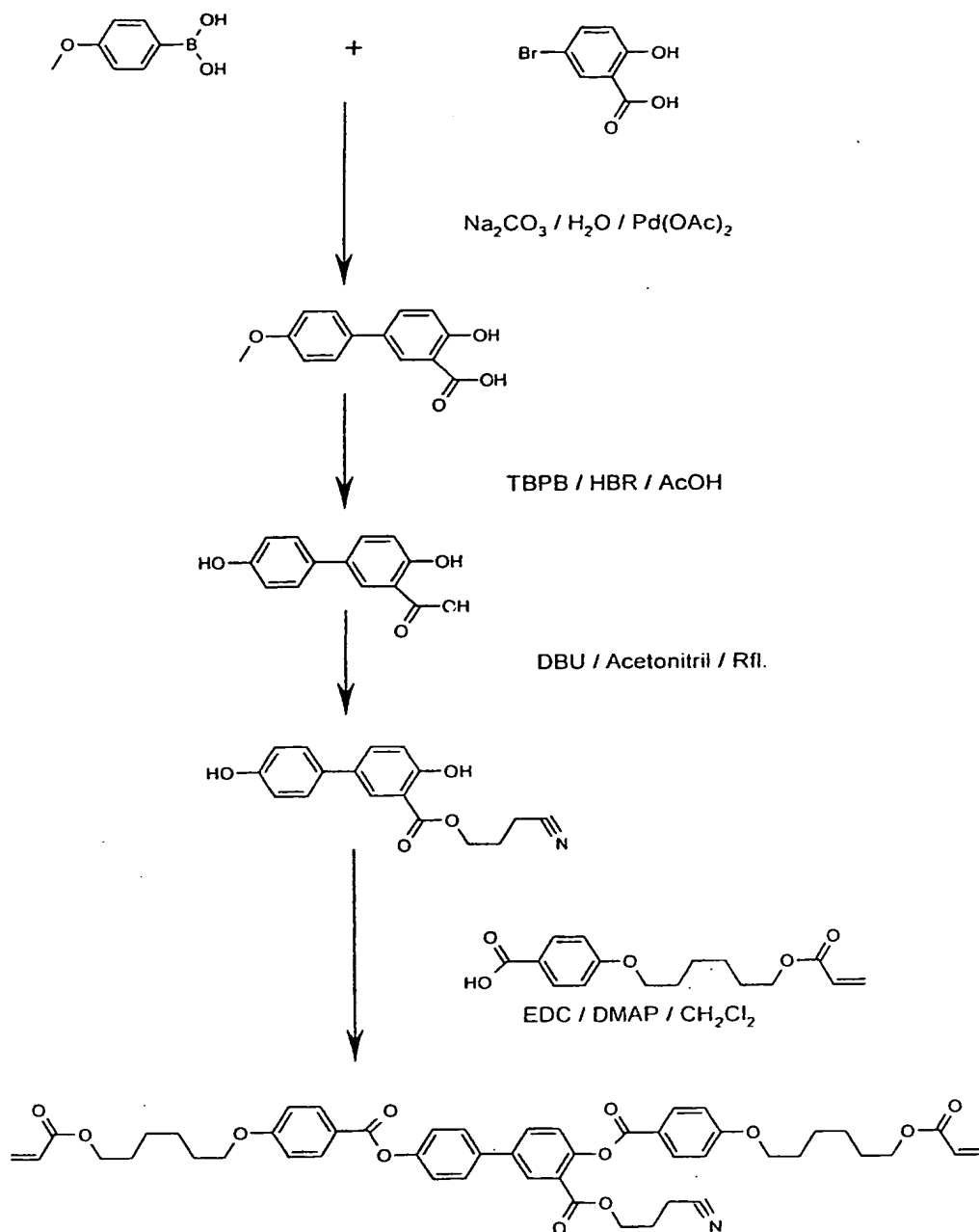
KI is potassium iodide

DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene

EDC is N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride

DMAP is 4-dimethylaminopyridine

Scheme 4



in which:

TBPB is tetrabutylphosphonium bromide

HBr is 48-% hydrobromic acid

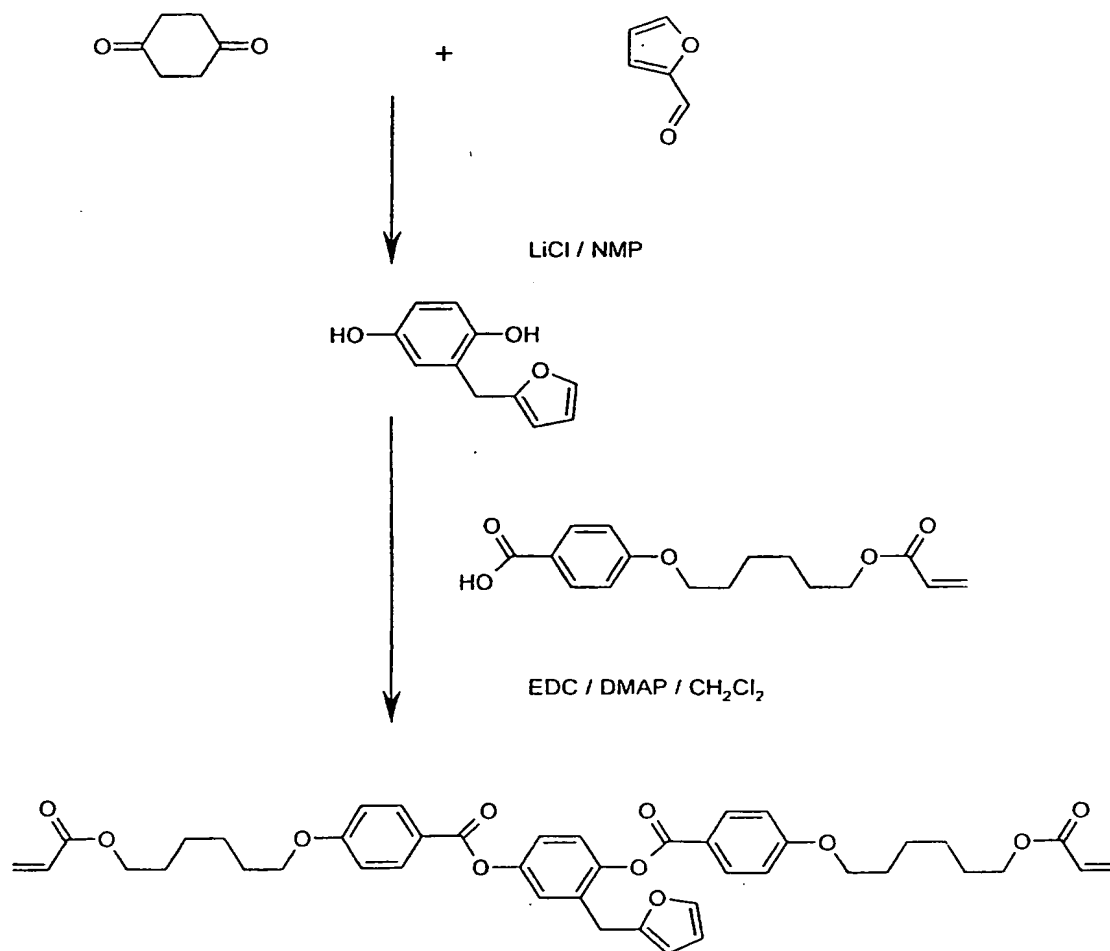
5 AcOH is acetic acid

DBU is 1,8-diazabicyclo[5.4.0]undec-7-ene

EDC is N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride

DMAP is 4-dimethylaminopyridine

Scheme 5



in which :

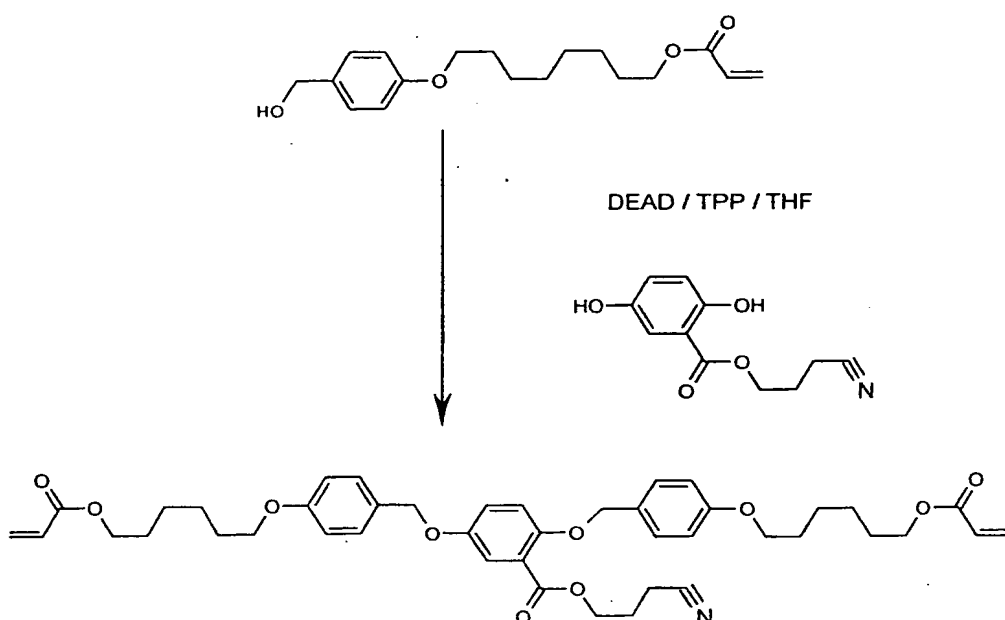
NMP is 1,3-dimethyl-2-imidazolidinone

EDC is N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride

5 DMAP is 4-dimethylaminopyridine

Scheme 6

10

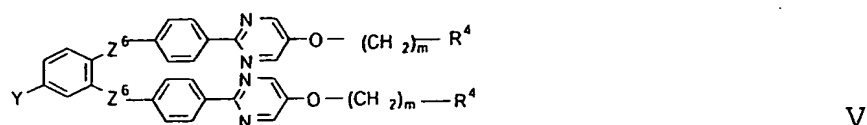
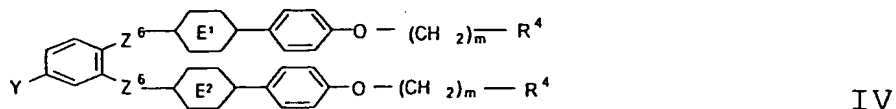
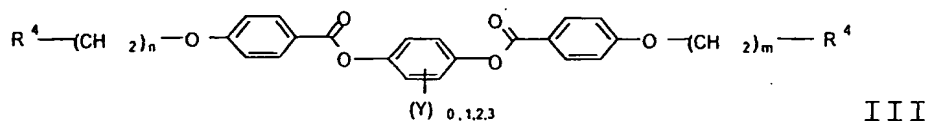


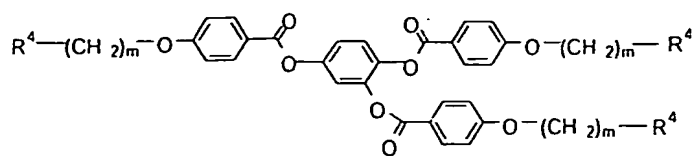
Suitable starting materials used in the preparation of the compounds of the present invention include, amongst others, phenyl and biphenyl carboxylic acid compounds as well as 1,4-cyclohexanedione. The compounds of the invention are preferably prepared by forming a ring that includes a lateral group prior to linking the mesogenic residues. Alternatively, the compounds may be prepared by forming a ring that includes a polymerisable mesogenic residue prior to linking the lateral group. A second aspect of the invention therefore provides a method of preparation of a compound of formula (I), the method comprising forming a ring that includes a lateral

group and subsequently linking the mesogenic residue thereto. The mesogenic residues G^1 and G^2 are preferably attached simultaneously. As indicated above, it is especially preferred that the mesogenic residues G^1 and G^2 are identical.

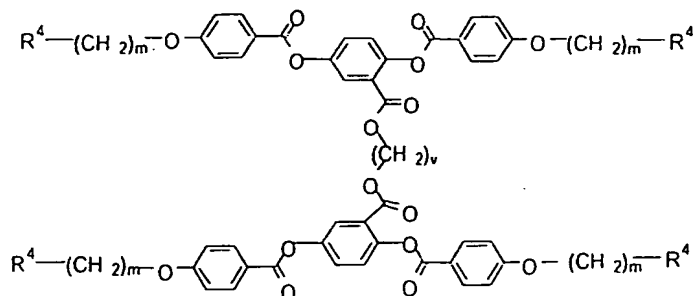
It will be appreciated that the compounds of the invention may be used in the preparation of liquid crystalline mixtures. Such mixtures may be prepared by admixing a compound of formula (II) with one or more additional components. An organic solvent may also be used in the preparation of these mixtures. A third aspect of the invention therefore provides a liquid crystalline mixture comprising a compound of formula (I) and one or more additional components. The one or more additional components present in the liquid crystalline mixture may be further compounds of formula (I), other mesogenic compounds, compounds that are compatible with a mesogenic molecular architecture or chiral dopants for the introduction of helical pitch. The LCP mixture may also include a suitable organic solvent. Examples of solvents that may be used in the preparation of such liquid crystalline mixtures include anisole, caprolactone, cyclohexanone, methyl ethyl ketone, methyl propyl ketone and the like.

Examples of additional components that may be used in the preparation of liquid crystalline LCP mixtures according to the third aspect of the invention include those compounds represented by formulae III to X.

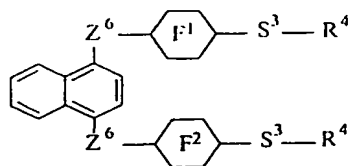




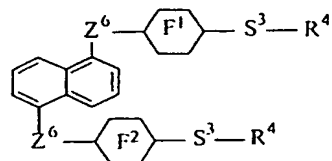
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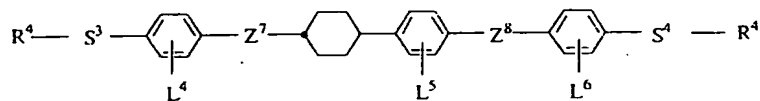
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VIII



IX

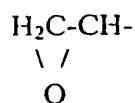


X

in which

R^4 is selected from the group consisting $CH_2=CH-O-$, $CH_2=CH-COO-$, $CH_2=C(CH_3)-COO-$, $CH_2=C(Cl)-COO-$ and

10



S^3, S^4 independently represent $-(CH_2)_n-$ or $-O(CH_2)_n-$

- E^1, E^2 are independently selected from the group consisting 1,4-phenylene, trans-1,4-cyclohexylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl and trans 1,4-cyclohexylene-1,4-phenylene;
- F^1, F^2 are independently selected from the group consisting 1,4-phenylene, and 2- or 3-fluoro-1,4-phenylene;
- L^4, L^5, L^6 are independently selected from the group consisting OH, C_1 - C_{20} -alkyl, C_1 - C_{20} -alkenyl, C_1 - C_{20} -alkoxy, C_1 - C_{20} -alkoxy-carbonyl, formyl, C_1 - C_{20} -alkylcarbonyl, C_1 - C_{20} -alkylcarbonyloxy, halogen, cyano and nitro;
- Z^6 is selected from the group consisting -COO-, -OOC-, -OCH₂-, -CH₂O-, -O(CH₂)₃-, -OOC(CH₂)₂- and -COO(CH₂)₃-;
- Z^7 is selected from the group consisting a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, -(CH₂)₄-, -O(CH₂)₃-, (CH₂)₃O- and -C≡C-;
- Z^8 is selected from the group consisting a single bond, -CH₂CH₂-, -CH₂O-, -OCH₂-, -COO-, -OOC-, and -C≡C-;
- Y is independently selected from the group consisting hydroxy, C_1 - C_{20} -alkyl, C_1 - C_{20} -alkenyl, C_1 - C_{20} -alkoxy, C_1 - C_{20} -alkoxycarbonyl, formyl-, C_1 - C_{20} -alkylcarbonyl, C_1 - C_{20} -alkylcarbonyloxy, fluoro, chloro, bromo, cyano and nitro;
- m is an integer having a value of from 2 to 20; and
- v is an integer having a value of from 2 to 12

The compounds of the invention may also be used in the formation of a LCP layer by casting a LCP compound according to the first aspect of the invention or a mixture according to the third aspect of the invention onto a substrate. A fourth aspect of the invention therefore provides a method forming a LCP network comprising forming a LCP layer including a compound of formula (I) and cross-linking the layer. Liquid crystalline mixtures according to the third aspect of the invention may also be used in the manufacture of LCP networks in a similar way.

The invention also includes, in a fifth aspect of the invention, a cross-linked LCP network comprising a compound of formula (I) in a cross-linked form. Cross-linked

LCP networks comprising a mixture according to the third aspect of the invention in cross-linked form may also be included in this aspect of the invention.

A sixth aspect of the invention provides the use of a compound of formula (I) in the preparation of an optical or an electro-optical device. The use, in the preparation of
5 an optical or electro-optical device, of liquid crystalline mixtures according to the third aspect of the invention is also included in this aspect of the invention.

An seventh aspect of the invention provides an optical or an electro-optical device comprising a compound of formula (I) in a cross-linked state. An optical or electro-optical device comprising a LCP liquid crystalline mixture in a cross-linked state
10 according to the third aspect of the invention is also included in this aspect of the invention.

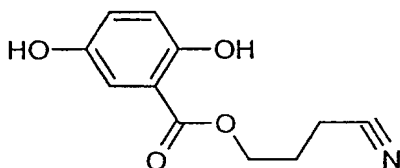
The invention will now be described with reference to the following non-limiting examples. These examples are provided by way of illustration only. Variations on these examples falling within the scope of the invention will be apparent to a skilled
15 person.

Examples

Example 1

Synthesis of 3-cyanopropyl 2,5-dihydroxybenzoate

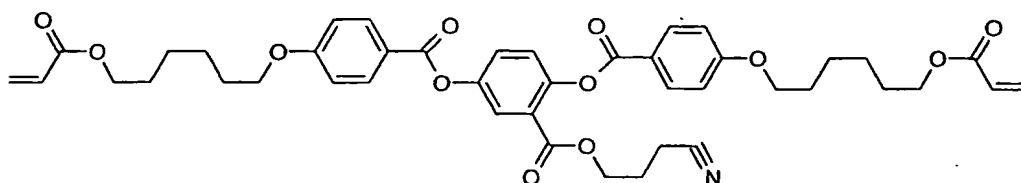
20



A mixture of 2,5-dihydroxybenzoic acid (4.6g; 30mmol), 1,8-diazabicyclo[5.4.0]
25 undec-7-ene (5.0g; 33mmol), 4-bromobutyronitrile (4.9g; 33mmol) and acetonitrile (70ml) was heated under reflux overnight. The reaction mixture was added to water (500ml) and extracted with ethyl acetate (3 x 100ml). The combined organic layers were washed with 1N-hydrochloric acid (150ml) and water (2 x 150ml). dried over magnesium sulphate and filtered. The organic solvent was then removed *in vacuo*. The
30 residue (6.2g) was recrystallised from ethyl acetate/hexane to yield 5.2g (78%) of the desired 3-cyanopropyl 2,5-dihydroxybenzoate.

Synthesis of 2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoic acid 3-cyanopropyl ester

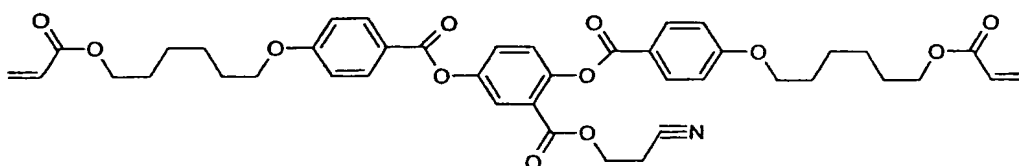
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- 10 A solution of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (6.5g; 39.9mmol) in dichloromethane (100ml) was added slowly to a solution of 3-cyanopropyl 2,5-dihydroxybenzoate (9.9g; 33.9mmol), 4-(6-acryloyloxyhexyloxy)-benzoic acid (5.7; 19.5mmol) and 4-dimethylaminopyridine (0.8g; 6.7mmol) in dichloromethane (60ml) at 0°C. The mixture was stirred at room temperature overnight.
- 15 It was then added to water (300ml) and extracted with dichloromethane (3 x 100ml). The combined organic layers were washed with water (2 x 130ml), dried over magnesium sulphate and filtered. The organic solvent was then removed *in vacuo*. The residue (14.0g) was purified by column flash chromatography on silica gel using toluene/ethyl acetate (85:15) as eluent, to yield 6.3g (60.6%) of 2,5-bis-[4-(6-acryloyloxy)hexyloxybenzoyloxy]benzoic acid 3-cyanopropyl ester. Mp = 42°C; Clp (N-I) = 63.7°C. This compound may be supercooled.
- 20

The following compounds were prepared in a similar way.

2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoic acid 2-cyanoethyl ester



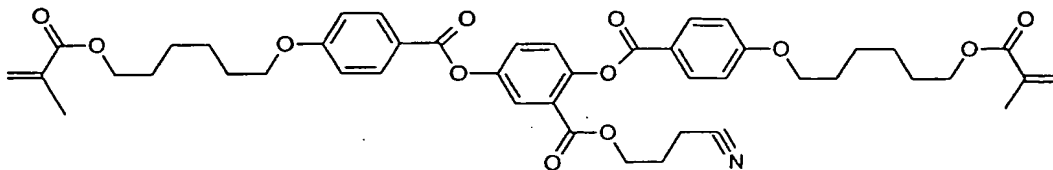
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Mp = 46.5°C; Clp (N-I) = 61°C

The compound may be supercooled.

30

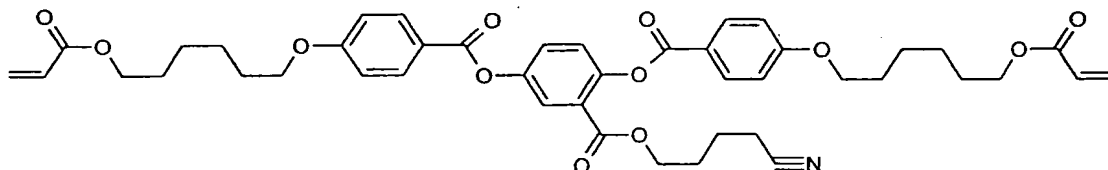
2,5-bis-[4-(6-(2-methacryloyloxy)hexyloxy)benzoyloxy]benzoic acid 3-cyanopropyl ester



Mp = 10°C; Clp (N-I) = 41.4°C

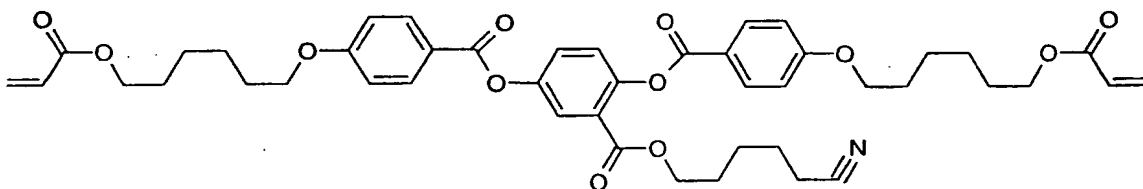
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2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoic acid 4-cyanobutyl ester



Mp = 79°C; Clp (N-I) = 56°C

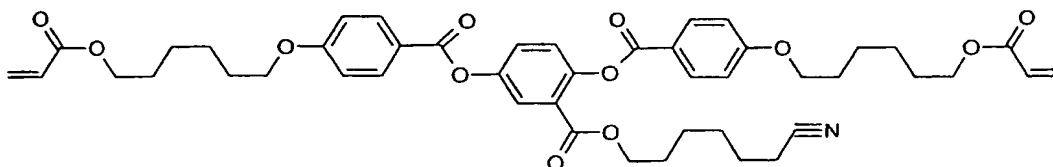
2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy] benzoic acid 5-cyanopentyl ester



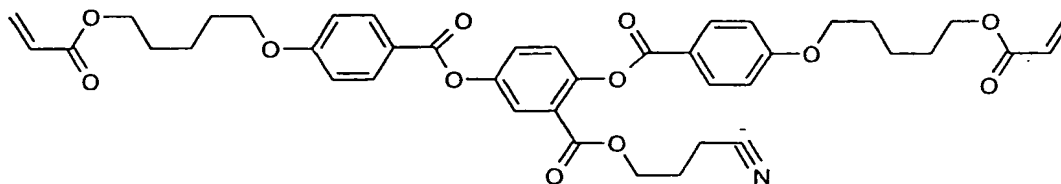
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Mp = 85°C; Clp (N-I) = 63.1°C

2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoic acid 6-cyanoethyl ester

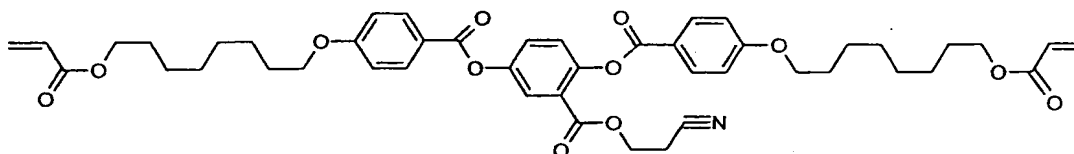


15 Mp = 57°C; Clp (N-I) = 58.2°C
The compound may be supercooled.

2,5-bis-[4-(5-acryloyloxypropyloxy)benzoyloxy]benzoic acid 3-cyanopropyl ester

5 Mp = 97°C; Clp (N-I) = 72.2°C

The compound may be supercooled.

2,5-bis-[4-(8-acryloyloxyoctyloxy)benzoyloxy]benzoic acid 3-cyanopropyl ester

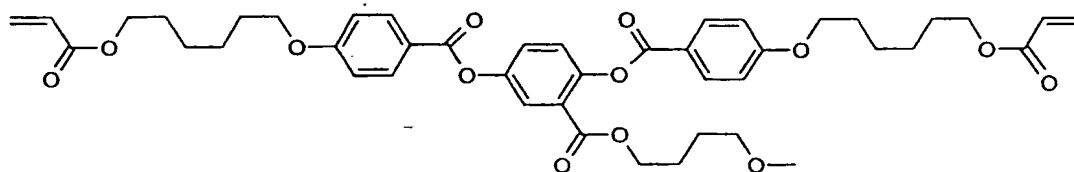
10

Mp = 63.5°C; Clp; (N-I) = 66°C

The compound may be supercooled.

2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoic acid 4-methoxybutyl ester

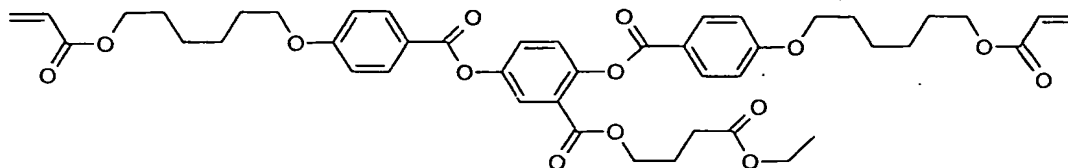
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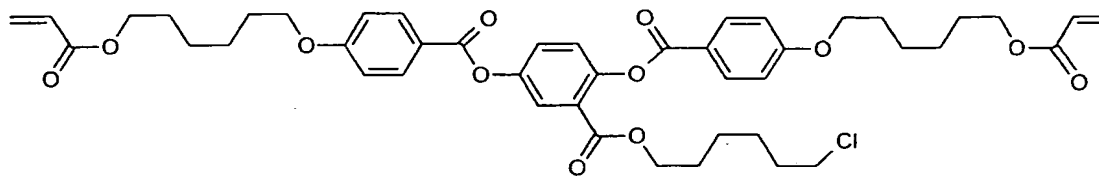
Clp (N-I) = 59°C

The compound may be supercooled.

[[3-(ethoxycarbonyl)propoxy]carbonyl]-p-phenylene bis[p-[6-(acryloyloxy)hexyloxy]benzoate]

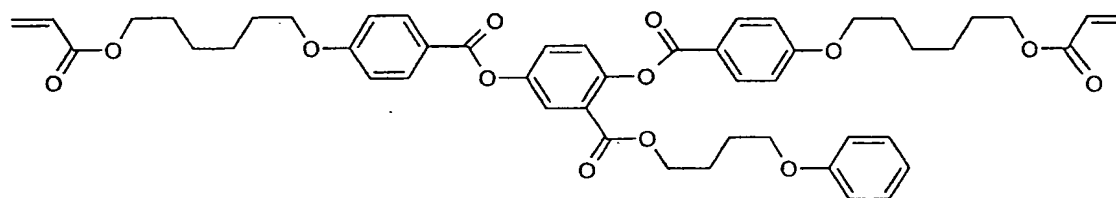


5 [[6-(chlorohexyl)oxy]carbonyl]-p-phenylene bis[p-[6-(acryloyloxy)hexyloxy]-benzoate]

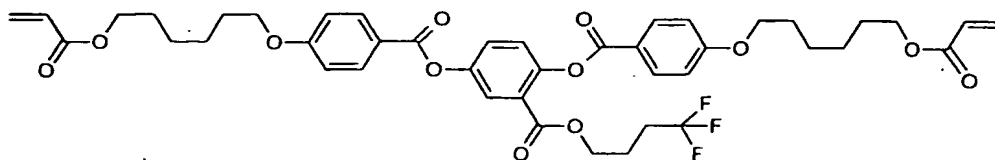


Mp = 44°C; Clp (N-I) = 62.6°C

10 [[4-phenoxybutoxy]carbonyl]-p-phenylene bis[p-[6-(acryloyloxy)hexyloxy]-benzoate]



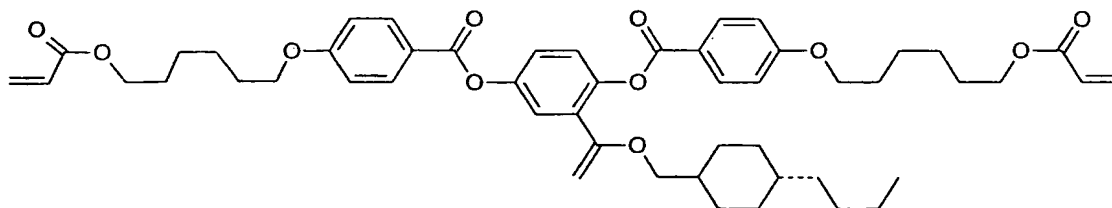
[(4,4,4-trifluorobutoxy)carbonyl]-p-phenylene bis[p-[6-(acryloyloxy)hexyloxy]-benzoate]



Mp = 69.7°C; Clp (N-I) = 55.1°C

- 5 The compound may be supercooled.

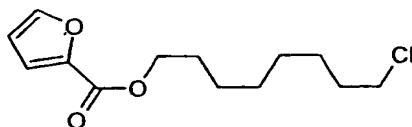
[trans-4-butylcyclohexyl)methoxycarbonyl]-p-phenylene bis[p-[6-(acryloyloxy)hexyl]oxy]-benzoate



- 10 Mp = 66°C; Clp (N-I) = 59.8°C. The compound may be supercooled

Example 2

Synthesis of 8-chlorooctyl 2-furancarboxylate



15

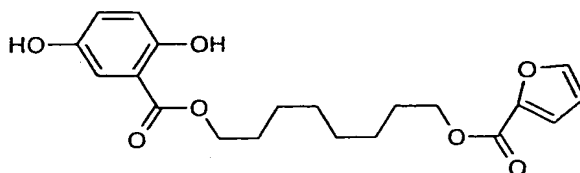
A solution of 2-furoyl chloride (6.5g; 50mmol) was added dropwise at 0°C to a solution of 8-chloro-1-octanol (6.6g; 40mmol) and pyridine (20g; 253mmol) and stirred at room temperature for 2h. The resulting mixture was added to a mixture of 1N-hydrochloric acid and ice (200ml) and extracted with ethyl acetate (3 x 80ml). The combined organic

- 20 layers were washed with saturated sodium chloride solution (2 x 80ml), dried over

magnesium sulphate and filtered. The organic solvent was removed *in vacuo* to give 8-chlorooctyl-2-furancarboxylate (9.7g) (94%) as an oil.

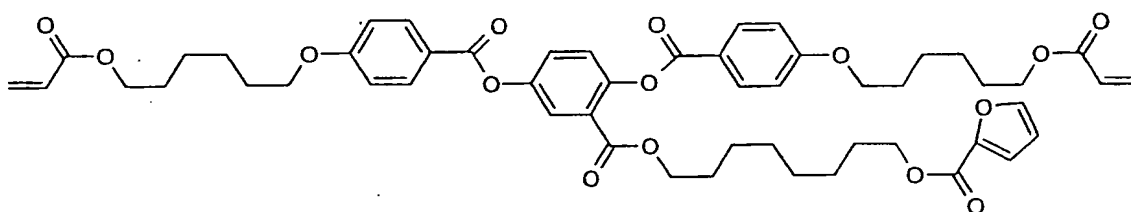
Synthesis of octamethylene 2,5-dihydroxybenzoate 2-furoate

5



A mixture of 2,5-dihydroxybenzoic acid (5.8 g; 37mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (5.7g; 37mmol), 8-chlorooctyl-2-furancarboxylate (9.7g; 37mmol), potassium iodide (7.8g; 47mmol) and acetonitrile (150ml) was heated, under reflux for 44h. The cooled reaction mixture was added to water (600ml) and extracted with ethyl acetate (3 x 150ml). The combined organic layers were washed with 1N-hydrochloric acid (150ml) and water (2 x 150ml), dried over magnesium sulphate and filtered. The solvent was then removed *in vacuo*. Recrystallisation of the residue (12.3g) from ethyl acetate/hexane gave 9.5g (68%) of octamethylene-2,5-dihydroxybenzoate-2-furoate.

Synthesis of furan-2-carboxylic acid 8-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxy}octyl ester



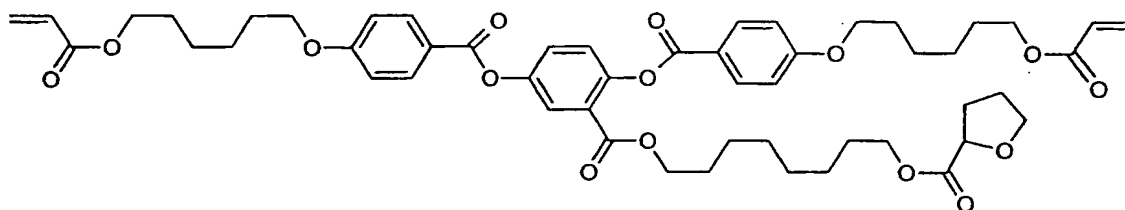
20 A solution of N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (8.9 g; 46.5mmol) in dichloromethane (140ml) was slowly added to a solution of octamethylene-2,5-dihydroxybenzoate-2-furoate (7.0g; 18.6mmol), 4-(6-acryloyl hexyloxy)benzoic acid (13.6g; 46.5mmol) and 4-dimethylaminopyridine (1.1 g;

- 9.3mmol) in dichloromethane (130ml) at 0°C. The mixture was stirred overnight at room temperature. The resulting solution was then added to water (600ml) and extracted with dichloromethane (3 x 250ml). The combined organic layers were washed with water (2 x 200ml), dried over magnesium sulphate and filtered. The solvent was removed in vacuo. The residue (21.0g) was purified by column flash chromatography on silica gel using toluene/ethyl acetate (93:7) as eluent, to give 8.3g (48,2%) of furan-2-carboxylic acid 8-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-benzoyloxy}octyl ester Mp = 36°C; Clp (N-I) = 41.2°C. The compound may be supercooled.

10

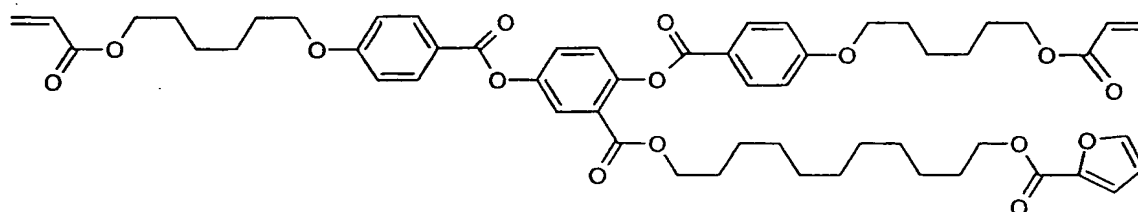
The following compounds were prepared in a similar manner.

(RS)-tetrahydrofuran-2-carboxylic acid 8-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxy}octyl ester



- 15 Clp (N-I) = 27°C

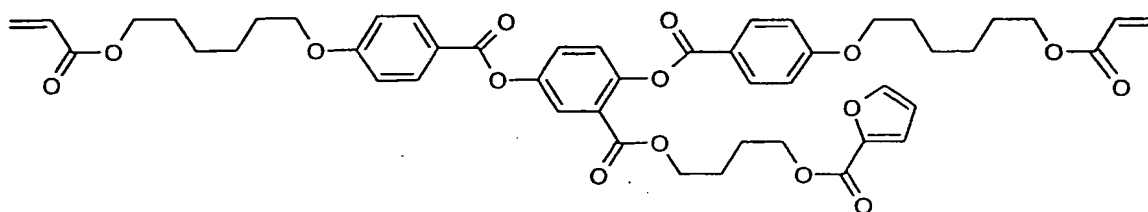
Furan-2-carboxylic acid 11-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxy}undecyl ester



Mp = 43.9°C; Clp (N-I) = 45.8°C

- 20 The compound may be supercooled.

Furan-2-carboxylic acid 4-{2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoyloxy}butyl ester

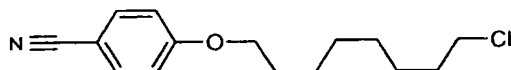


Clp (N-1) = 40.7°C

- 5 The compound may be supercooled.

Example 3

Synthesis of p-[(8-chlorooctyl)oxy]benzonitrile

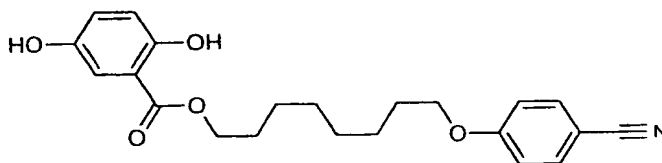


10

A solution of diethyl azodicarboxylate (7.3 g; 42mmol) and tetrahydrofuran (15ml) was added dropwise at 0°C to a solution of 4-hydroxybenzonitrile (4.2g; 35mmol), 8-chloro-1-octanol (6.9g; 42mmol), triphenylphosphine (11.0g; 42mmol) and tetrahydrofuran (70ml) and stirred at room temperature overnight. The reaction mixture was added to water (200ml) and extracted with ethyl acetate (3 x 100ml), dried over magnesium sulphate and filtered. The solvent was then removed *in vacuo*. The residue was purified by column flash chromatography on silica gel using toluene/ethyl acetate (97:3) as eluent, to give 8.8g (94%) of p-[(8-chlorooctyl)oxy] benzonitrile.

20

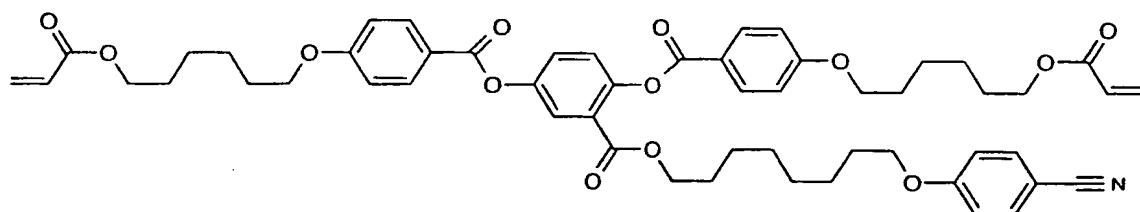
Synthesis of 8-(p-cyanophenoxy)octyl 2,5-dihydroxybenzoate



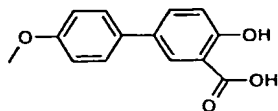
A mixture of 2,5-dihydroxybenzoic acid (4.2g; 27.5mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (4.2g; 27.5mmol), potassium iodide (41.0g; 247mmol),

p-[(8-chlorooctyl)oxy]benzonitrile (6.6g; 25mmol) and acetonitrile (100ml) was heated under reflux for 72h. The reaction mixture was cooled, poured into water (500ml) and extracted with ethyl acetate (3 x 150ml). The combined organic layers were washed with 1N-hydrochloric acid (150ml) and water (2 x 150ml), dried over magnesium sulphate and filtered. The solvent was removed *in vacuo*. The residue was purified by column flash chromatography on silica gel using a toluene/ethyl acetate 80:20 as eluent to give 8.0g (84%) of 8-(p-cyanophenoxy)octyl 2,5-dihydroxybenzoate.

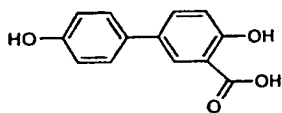
Synthesis of 2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoic acid 8-(4-cyanophenoxy)octyl ester



A solution of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (3.7g; 19.5mmol) in dichloromethane (60ml) was added slowly to a solution of 8-(p-cyanophenoxy)octyl-2,5-dihydroxybenzoate (3g; 7.8mmol), 4-(acryloyloxyhexyloxy)-benzoic acid (5.7g; 19.5mmol) and 4-dimethylaminopyridine (0.5g; 3.9mmol) in dichloromethane (80ml) at 0°C. The mixture was stirred overnight at room temperature. The resulting mixture was added to water (350ml) and extracted with dichloromethane (3 x 100ml). The combined organic layers were washed with water (2 x 100ml), dried over magnesium sulphate and filtered. The organic solvent was removed *in vacuo*. The residue (9.0g) was purified by flash chromatography using a silica gel column and toluene/ethyl acetate (98:2) as eluent, to give 4.6g (63%) of 2,5-bis-[4-(6-acryloyloxyhexyloxy)benzoyloxy]benzoic acid 8-(4-cyanophenoxy)octyl ester. Mp = 54.5°C; Clp (N-I) = 78.4°C; (S_A-N) = 43.5°C. The compound may be supercooled.

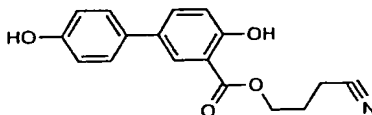
Example 4**Synthesis of 4-hydroxy-4'-methoxy-3-biphenylcarboxylic acid**

- 5 Palladium(II)acetate (55mg; 0.23mmol) was added under argon to a mixture of 5-bromosalicylic acid (5.4g; 22.4mmol), sodium carbonate (7.2g; 68.1mmol) and 4-methoxyboronic acid (3.8g; 25mmol) in water (125ml). The reaction mixture was stirred at room temperature for 1h. The resulting slurry was dissolved in hot water (1300ml) and filtered to give a filtrate and a precipitate. The filtrate was acidified with
- 10 hydrochloric acid. The precipitate was washed with water and dried in vacuo to give 5.3g (95%) of 4-hydroxy-4'-methoxy-3-biphenylcarboxylic acid.

Synthesis of 4,4'-dihydroxy-3-biphenylcarboxylic acid

- A solution of 4-hydroxy-4'-methoxy-3-biphenylcarboxylic acid (5.3g; 21.6mmol),
- 15 tetrabutylphosphonium bromide (0.8g; 2.3mmol), acetic acid (35ml) and hydrobromic acid (35ml of a 48% solution) was heated at reflux for 6h. The reaction mixture was cooled and poured into water (400ml). The resulting precipitate was isolated and recrystallised from ethyl acetate to give 2.4g (47%) of 4,4'-dihydroxy-3-biphenylcarboxylic acid.

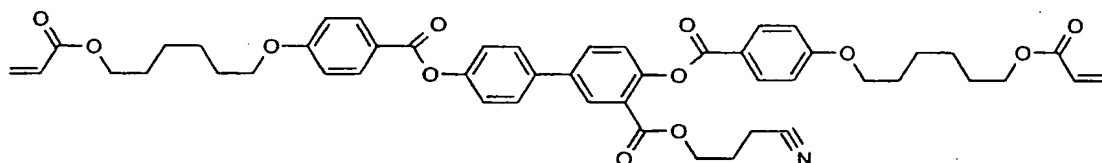
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Synthesis of 3-cyanopropyl-4,4'-dihydroxy-3-biphenylcarboxylate

A mixture of 4,4'-dihydroxy-3-biphenylcarboxylic acid (2.3g; 10mmol), 1,8-diazabicyclo[5.4.0]undec-7-ene (1.7g; 11.2mmol), 4-bromobutyronitrile (1.7g; 11.2mmol)

and N,N-dimethylformamide (40ml) was heated at 75°C for 4h. The reaction mixture was cooled, poured into water (300ml) and extracted with ethyl acetate (3 x 100ml). The combined organic layers were washed with 1N-hydrochloric acid (150ml) and with water (2 x 100ml), dried over magnesium sulphate and filtered. The organic solvent was removed *in vacuo*. The residue (3.0g) was purified by flash chromatography using a silica gel column and toluene/ethyl acetate (97:3) as eluent to give 2.1g (70%) of 3-cyanopropyl-4,4'-dihydroxy-3-biphenylcarboxylate.

10 Synthesis of 3-[(3-cyanopropoxy)carbonyl]-4,4'-biphenylene bis[p-[6-(acryloyloxy)hexyloxy]benzoate]

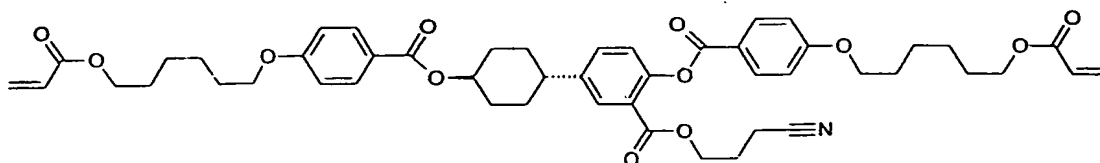


A solution of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (2.9g; 15.4mmol) in dichloromethane (50ml) was slowly added to a solution of 3-cyanopropyl-4,4'-dihydroxy-3-biphenylcarboxylate (2.1g; 7.1mmol), 4-(6-acryloylhexyloxy)benzoic acid (4.5g; 15.4mmol) and 4-dimethylaminopyridine (0.5g; 3.9mmol) in dichloromethane (80ml) at 0°C. The mixture was stirred at room temperature overnight. The resulting mixture was added to water (300ml) and extracted with dichloromethane (3 x 100ml). The combined organic layers were washed with water (2 x 100ml), dried over magnesium sulphate and filtered. The organic solvent was removed *in vacuo*. The residue (6.3g) was purified by flash chromatography using a silica gel column and toluene/ethyl acetate (90:10) as eluent, to yield 1.3g (20%) of 3-[(3-cyanopropoxy)carbonyl]-4,4'-biphenylene bis[p-[6-(acryloyloxy)hexyloxy]benzoate].

25 Mp = 85.5°C; Clp (N-I) = 154.5°C. The compound may be supercooled.

The following compound was prepared in a similar way:

3-[(3-cyanopropoxy)carbonyl]-4-(trans-4-cyclohexyl)-phenyl bis[p-(6-(acryloyloxy)hexyloxy)-benzoate]

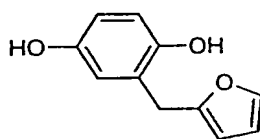


Mp = 98°C; Clp (N-I) = 140°C.

5

Example 5

Synthesis of 2-furfurylhydroquinone

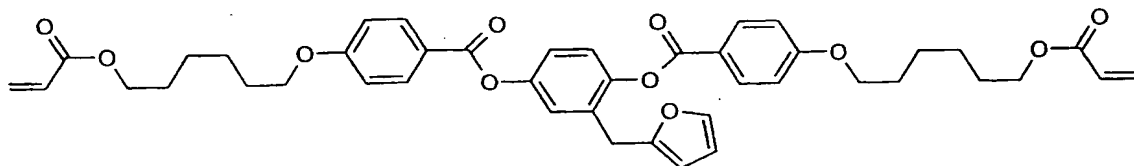


10

A mixture of 1,4-cyclohexanedione (5.6g; 50mmol), furan-2-carbaldehyde (4.8g; 50mmol) and anhydrous lithium chloride (2.1g; 50mmol) in 1,3-dimethyl-2-imidazolidinone (20ml) was heated with stirring over an oil bath at atmospheric pressure. The temperature of the bath was maintained at 165°C for 1h. The cooled reaction mixture was poured into water (300ml) and extracted with ethyl acetate (2 x 150ml). The combined organic layers were washed with water (2 x 100ml), dried over magnesium sulphate and filtered. The organic solvent was removed in vacuo. The residue (9.4g) was purified by flash chromatography using a silica gel column and toluene/ethyl acetate (90:10) as eluent, to give 6.7g (70%) of 3-furfurylhydroquinone.

20

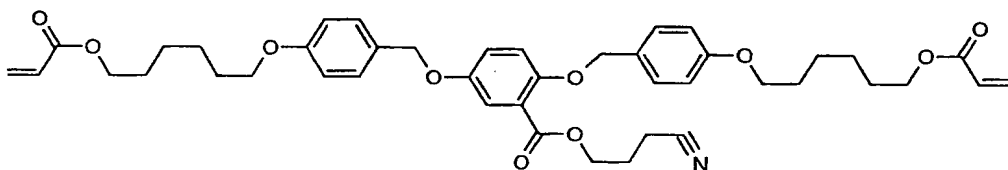
Synthesis of 4-(6-(acryloyloxyhexyloxy)benzoic acid
4-[4-(6-(acryloyloxyhexyloxy)benzoyloxy]3-furan-2-ylmethylphenyl ester



A solution of N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (8.8g; 46mmol) in dichloromethane (160ml) was added slowly to a solution of 2-furfurylhydroquinone (3.5g; 18.4mmol), 4-(6-acryloyloxyhexyloxy)benzoic acid (13.4g; 46mmol) and 4-dimethylaminopyridine (0.5g; 3.9mmol) in dichloromethane (50ml) at 0°C. The reaction mixture was stirred at room temperature overnight, added to water (350ml) and extracted with dichloromethane (3 x 100ml). The combined organic layers were washed with water (2 x 100ml) dried over magnesium sulphate and filtered. The organic solvent was removed *in vacuo*. The residue (18.6g) was purified by flash chromatography using a silica gel column and toluene/ethyl acetate (95:5) as eluent and recrystallised from ethyl acetate/hexane to give 6.4g (47%) of 4-(6-acryloyloxyhexyloxy)benzoic acid 4-[4-(6-acryloyloxyhexyloxy)benzoyloxy]-3-furan-2-yl methylphenyl ester. Mp = 65°C Clp (N-I) = 51°C. The compound may be supercooled.

15 Example 6

Synthesis of [[(3-cyanopropoxy)carbonyl]-p-phenylene]bis[oxymethylene-p-phenyleneoxyhexamethylene] diacrylate

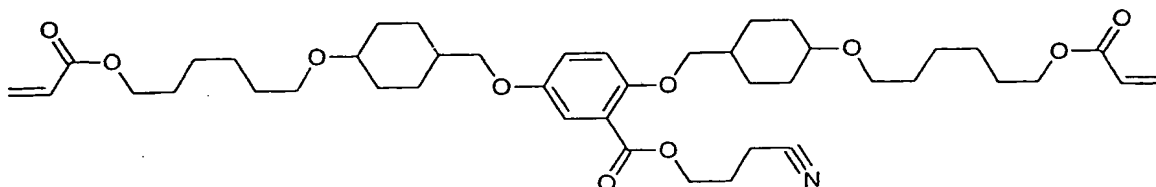


20 A solution of diethyl azodicarboxylate (4.2g; 24mmol) and tetrahydrofuran (20ml) was added dropwise at 0°C, to a solution of triphenylphosphine (6.4g; 24mmol) into tetrahydrofuran (40ml), the salt mixture was stirred for 2h at 0°C. After the salt mixture was added slowly at 0°C to a solution of 6-[(α-hydroxy-p-tolyl)oxy]hexyl acrylate (3.1g; 10mmol), 3-cyanopropyl-2,5-dihydroxybenzoate (2.2; 10mmol) and tetrahydrofuran (60ml), stirred at room temperature overnight. The reaction mixture was added to water (400ml) and extracted with ethyl acetate (3 x 200ml). The combined organic layers were washed with water (2 x 200ml), dried over magnesium sulphate, filtered and then evaporated down under reduced pressure. The residue (16.0g) was purified by column

flash chromatography on silica gel using a 95:5 toluene / ethyl acetate mixture as eluent. to yield 2.3g (31%) of the desired ether.

The following compound may be synthesised using a similar method:

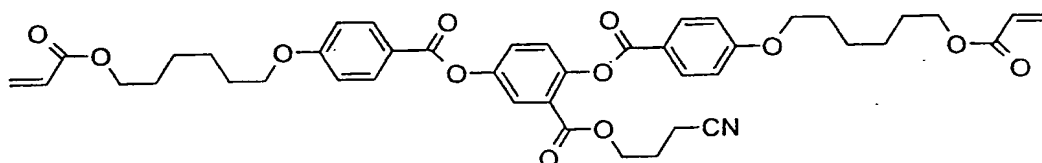
- 5 **[[[3-cyanopropoxy)carbonyl]-p-phenylene]bis[oxymethylene(trans-1,4-cyclohexylene)oxyhexamethylene] diacrylate**



10 Example 7

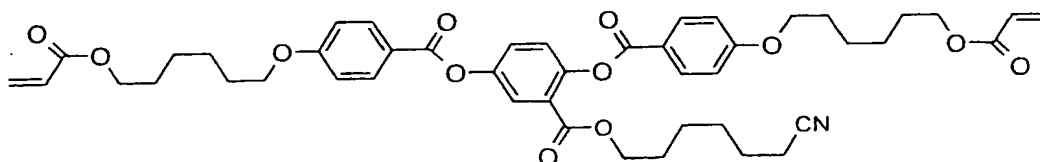
Preparation of nematic LCP Films

- (i) A mixture of the following components in anisole was prepared:
70wt% of



15

30wt% of



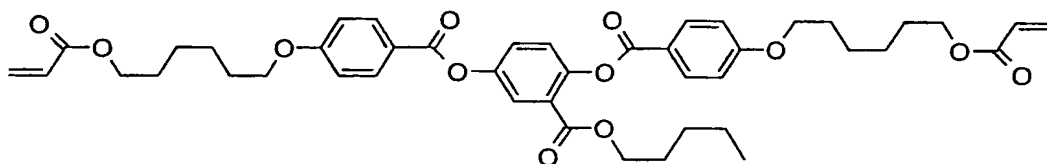
- 1000ppm of a Tinuvin 123 stabiliser and 500ppm of a 2,6-di-(t-butyl)-4-hydroxytoluene
20 (BHT) inhibitor were added to this mixture. 500ppm of an Irgacure 369 polymerisation

initiator (commercially available from Ciba Geigy, Basle, Switzerland) was added. The mixture was stirred at room temperature and then spincoated on a glass plate having an orientation layer to form an LCP film of approximately 800nm in thickness. This film was dried at 50°C for 1 or 2 minutes and photopolymerised by irradiation with UV light for approximately 5 minutes at room temperature in a N₂ atmosphere using a mercury lamp.

The film exhibits a nematic mesophase at room temperature. In addition this film exhibits a tilt angle of about 10° relative to the plane of the substrate, as shown by ellipsometric measurements. The non-polymerised film exhibits an excellent super cooling behaviour.

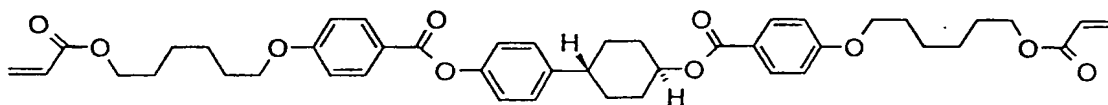
(ii) A mixture of the following components in anisole was prepared according to procedure (i) above.

60wt% of



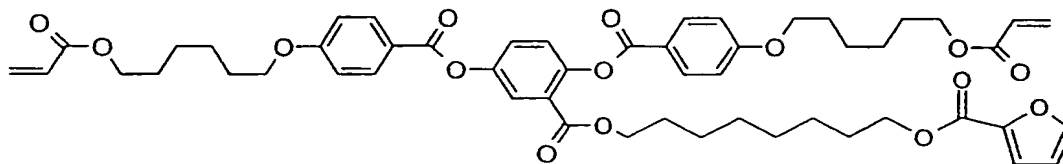
15

20wt% of



20

10wt% of

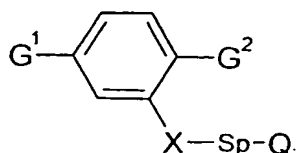


and 10 wt% of 1,4-butanediol diacrylate (Aldrich)

The nematic film formed exhibits a well oriented nematic mesophase at room temperature with a clearing point of 80°C. In addition this film exhibits a tilt angle of
5 about 1° relative to the plane of the substrate, as shown by ellipsometric measurements.

Claims

1. A compound of formula (I)



5 wherein

G^1 and G^2 independently represent a polymerisable mesogenic residue

X represents a group selected from the group consisting $-CH_2-$, $-O-$, $-CO-$, $-COO-$, $-OOC-$, $-CONR'-$, $-OCOO-$ and $-OCONR'$;

10 Sp represents a group of the formula $-(CH_2)_p-$ in which p is an integer of 1 to 18 and in which one or two non adjacent $-CH_2-$ groups are optionally replaced by $-CH=CH-$; or in which one or two $-CH_2-$ groups may be replaced by one or two groups selected from the group consisting $-CH_2-$, $-O-$, $-CO-$, $-COO-$, $-OOC-$, $-CONR'-$, $-OCOO-$ and $-OCONR'-$ with the
15 proviso that firstly the spacer group does not contain two adjacent heteroatoms and secondly when X is $-CH_2-$, p can also have a value of 0;

Q represents a polar group selected from $-CN$, $-COR$, $-COOR$, $-OCOR$, $-CONR'R$, $-NR'COR$, $-OCOOR$, $-OCONR'R$, $-NR'COOR$, F, Cl, $-CF_3$, $-OCF_3$ or $-OR$ or a cyclic group which is unsubstituted or optionally
20 substituted by a group selected from a lower alkyl, lower alkenyl, lower alkoxy, lower alkenyloxy, halogen, $-CN$, $-COR''$, $-COOR''$, $-OCOR''$, $-CONR'R''$, $-NR'COR''$, $-OCOOR''$, $-OCONR'R''$, $-NR'COOR''$, $-CF_3$, and $-OCF_3$;

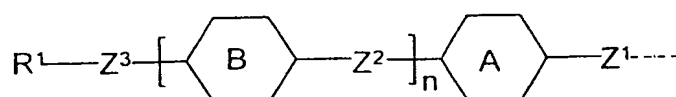
25 where

R represents hydrogen, a lower alkyl, a lower alkenyl or a cyclic group as defined above; and

R' is hydrogen, a lower alkyl or a lower alkenyl group

R'' represents a lower alkyl or a lower alkenyl group.

2. A compound according to Claim 1, in which G¹ and G² are the same.
3. A compound according to Claim 1 or Claim 2, in which X is selected from -CH₂-, -
- 5 O-, -COO- and -OOC-.
4. A compound according to any one of claims 1 to 3, in which the integer p of the Sp group has a value of from 1 to 11.
5. A compound according to any one of the preceding claims, in which no more than one -CH₂- moiety of the Sp group is replaced by -CH=CH-, -O-, CO-, -COO-, -OOC-,
- 10 -CONR', -OCOO-, -OCONR'.
6. A compound according to any one of the preceding claims, in which Q is selected from -CN-, -COOR, -OCOR, Cl, -CF₃, -OCF₃, -OR or a cyclic group.
7. A compound according to any one of the preceding claims, in which the cyclic group is selected from a five or six membered saturated or unsaturated, isocyclic or
- 15 heterocyclic moiety.
8. A compound according to any one of the preceding claims in which the cyclic group is optionally substituted by a group selected from a lower alkyl, lower alkoxy, F, Cl, -CN, -COOR'', -OCOR'', -OCF₃, OR'', in which R'' is lower alkyl
9. A compound according to any one of the preceding claims in which the mesogenic residues G¹ and G² are of formula II
- 20

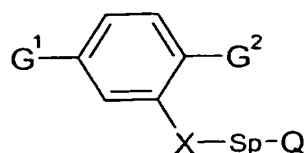


wherein

- A and B independently represent 1,4-phenylene, pyridine-2,5-diyl, pyrimidine-2,5-diyl, trans-1,4-cyclohexylene or trans-1,3-dioxane-1,4-diyl; optionally substituted with a halogen, -CN, a lower alkyl, lower alkenyl, lower alkoxy or lower alkenyloxy group;
- 25

n is 1 or 0,

- Z^1 and Z^2 independently represent a single bond, -COO-, -OOC-, -CH₂-CH₂-, -CH₂O-, -OCH₂-, -CH=CH-, -C≡C-, -(CH₂)₄-, or -(CH₂)₃O-;
- 5 Z^3 represents a group of formula -(CH₂)_pX- in which one or two non adjacent -CH₂- groups may be optionally replaced by -CH=CH- or in which one or two -CH₂- groups may be replaced by one or two groups selected from the group consisting -CH₂-, -O-, CO-, -COO-, -OOC-, -CONR'-, -OCOO- and -OCONR' with the proviso that firstly the spacer group does not contain two adjacent heteroatoms and secondly when X is -CH₂-, p can also have a value of 0;
- 10 wherein
p is an integer having a value of 1 to 12; and
X is selected from the group consisting -CH₂-, -O-, CO-, -COO-, -OOC-,
15 -CONR'-, -OCOO- and -OCONR';
- R^1 represents a polymerisable group selected from CH₂=C(Ph)-, CH₂=CW-COO-, CH₂=CH-COO-Ph-, CH₂=CW-CO-NH-, CH₂=CH-O-, CH₂=CH-OOC-, Ph-CH=CH-, CH₂=CH-Ph-, CH₂=CH-Ph-O-,
20 R³-Ph-CH=CH-COO-, R³-OOC-CH=CH-Ph-O- or 2-W-epoxyethyl
in which
W represents H, Cl, Ph or a lower alkyl,
R³ represents a lower alkyl or with the proviso that when R³ is attached to a 1,4-phenylene group (-Ph-) it may also represent
25 hydrogen or a lower alkoxy.
10. A compound according to Claim 9, in which Z^1 and Z^2 are selected from a single bond, -COO-, -OOC-, -CH₂-CH₂-, -CH₂O-, -OCH₂-, -CH=CH- and -C≡C-.
11. A compound according to Claim 9 or Claim 10, in which R¹ is selected from CH₂=CW-, CH₂=CW-COO- and CH₂=CH-O-.
- 30 12. A LCP mixture comprising a compound of formula (I)



wherein

G^1 and G^2 independently represent a polymerisable mesogenic residue

5 X is selected from the group consisting of $-CH_2-$, $-O-$, $-CO-$, $-COO-$, $-OOC-$, $-CONR'-$, $-OCOO-$ and $-OCONR'$;

10 Sp represents a group of the formula $-(CH_2)_p-$ in which p is an integer of 1 to 18 and in which one or two non adjacent $-CH_2-$ groups are optionally replaced by $-CH=CH-$; or in which one or two $-CH_2-$ groups may be replaced by one or two groups selected from $-CH_2-$, $-O-$, $CO-$, $-COO-$, $-OOC-$, $-CONR'-$, $-OCOO-$, $-OCONR'$ with the proviso that firstly the spacer group does not contain two adjacent heteroatoms and secondly when X is $-CH_2-$, p can also have a value of 0;

15 Q represents a a polar group selected from $-CN$, $-COR$, $-COOR$, $-OCOR$, $-CONR'R$, $-NR'COR$, $-OCOOR$, $-OCONR'R$, $-NR'COOR$, F, Cl, $-CF_3$, $-OCF_3$ or $-OR$ or a cyclic group which is unsubstituted or optionally substituted by a group selected from a lower alkyl, lower alkenyl, lower alkoxy, lower alkenyloxy, halogen, $-CN$, $-COR''$, $-COOR''$, $-OCOR''$, $-CONR'R''$, $-NR'COR''$, $-OCOOR''$, $-OCONR'R''$, $-NR'COOR''$, $-CF_3$, and $-OCF_3$;

where

25 R represents hydrogen, a lower alkyl, a lower alkenyl or a cyclic group as defined above; and

R' is hydrogen, a lower alkyl or a lower alkenyl group

R'' represents a lower alkyl or a lower alkenyl group.

and one or more additional suitable components.

13. A LCP network comprising a compound according to any one of claims 1 to 11 or a mixture according to Claim 12 in cross-linked or polymerised form.
14. Use of a compound according to any one of claims 1 to 11, or a mixture according to Claim 12, in the manufacture of an optical or an electro-optical device.
- 5 15. An optical or electro-optical device including a compound according to any one of claims 1 to 11 or a mixture according to Claim 12 in cross-linked or polymerised form.

INTERNATIONAL SEARCH REPORT

In National Application No

PCT/IB 00/00098

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C69/92 C09K19/20 C09K19/34 C09K19/38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09K C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	WO 00 04110 A (ROLIC AG) 27 January 2000 (2000-01-27) examples 4,5	1-15
Y,P	WO 99 37735 A (BUHECKER RICHARD ;ROLIC AG (CH); BENECKE CARSTEN (DE); MARCK GUY) 29 July 1999 (1999-07-29) page 9, line 14 -page 10, line 25	1-15
Y,P	WO 99 64924 A (SCHADT MARTIN ;ROLIC AG (CH); SEIBERLE HUBERT (DE)) 16 December 1999 (1999-12-16) example 1	1-15

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

19 April 2000

Date of mailing of the international search report

11. 05. 00

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
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Authorized officer

Boulon, A

INTERNATIONAL SEARCH REPORT

national application No.
PCT/IB 00/00098

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 1-15 relate to an extremely large number of possible compounds. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds prepared in the examples 1-7 and closely related homologous compounds

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as IPEA is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure."

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. l. Application No
PCT/IB 00/00098

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 0004110 A	27-01-2000	NONE	
WO 9937735 A	29-07-1999	NONE	
WO 9964924 A	16-12-1999	NONE	